



Modern Superabsorbent Polymer Technology

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COMMERCIAL PROCESSES FOR THE MANUFACTURE OF SUPERABSORBENT POLYMERS

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3.1. INTRODUCTION

Commercial superabsorbent polymers are partially neutralized polymers of acrylic acid that have been lightly crosslinked. The largest share of superabsorbent products is used in disposable baby diapers, with smaller quantities being used for adult incontinent devices and feminine hygiene pads. They are sold on the basis of their ability to prevent leakage in disposable personal hygiene articles. The polymer properties discussed most often for these applications are the swelling capacity of the polymer for urine (about 20–40 mL of urine per gram of polymer) and the modulus or ability of the polymer to resist deformation under an applied load (swelling under load).¹ Swelling and modulus have been treated,² based on the approaches of Flory³ and Mark and Erman,⁴ in terms of characteristic polymer properties.

The global market for superabsorbent polymers has grown and changed dramatically in the last 10 years as superabsorbents have replaced fluff pulp in diapers and other personal hygiene articles. Worldwide superabsorbent polymer production capacity (Table 3.1) grew from only a few million metric tons in 1985 to greater than 700 million tons in 1995.⁵ The North American market is maturing, evidence for which is the desire to exit the business of one of the early major manufacturers in the United States, The Nalco Chemical Co.,⁶ although market penetration is still

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Table 3.1. Worldwide production capacity for producers of superabsorbent polymer (thousand metric tons [t])

Producer	1986	1989	1992	1995	1996	1998 ^a
Allied Colloids	2.0	2.0	11.4	15.5	15.5	30.9
AMCOL Int. (Chemdal)	—	20.0	20.0	110.0	120.0	120.0
Arakawa	4.0	4.0	6.0	6.0	6.0	6.0
Atochem	—	5.0	8.0	9.0	12.0	12.0
Dow Chemical	22.7	46.4	60.0	90.0	90.0	120.0
U.S.	22.7	36.4	50.0	50.0	50.0	80.0 ^a
Europe	—	10.0	10.0	40.0	40.0	40.0
Formosa Plastics	—	0	6.0	12.0	12.0	12.0
Hoechst	—	29.0	55.0	97.0	97.0	97.0
U.S. (Hoechst Celanese)	—	24.0	40.0	69.0	69.0	69.0
Europe (Casella)	—	5.0	15.0	28.0	28.0	28.0
Kao Soap	—	5.0	10.0	10.0	10.0	10.0
Kolon	—	—	—	12.0	12.0	24.0
Mitsubishi	—	0	10.0	10.0	10.0	10.0
Nalco ^b	—	20.0	40.0	45.5	45.5	45.5
Nippon Shokubai	15.0	37.9	84.0	131.0	141.0	141.0
U.S. (NA Industries)	—	6.0	12.0	30.0	36.0	36.0
Europe (BASF)	—	0.4	12.0	20.0	24.0	24.0
Japan	15.0	31.5	60.0	81.0	81.0	81.0
Nippon Synthetic ^c	—	3.0	4.5	6.8	10.0	10.0
Sanyo	8.0	17.0	20.0	50.0	55.0	55.0
Sekisui	—	0	3.0	6.0	6.0	6.0
SNF	—	0	0	2.0	7.0	22.0 ^d
Stockhausen	—	50.0	79.5	110.9	110.9	110.9
U.S.	—	20.0	29.5	55.5	55.5	55.5
Europe	—	30.0	50.0	55.5	55.5	55.5
Sumitomo	3.1	5.6	8.0	22.0	32.0 ^e	59.0 ^f
Toa Gosei	—	0	10.0	10.0	10.0	10.0
Total	54.8	245.9	435.5	755.6	801.8	901.3

Data for 1992–1998 are from TranTech Consultants Inc. (TranTech began compiling their ChemPlan database for SAP in 1991.) Data for 1986 and 1989 are from The Dow Chemical Co. internal market studies.

^aIncludes 30,000 t potential capacity at low additional cost.

^bAcquired by Stockhausen in 1996.

^cTransferred technology and marketing rights to Mitsubishi in April 1996.

^dHas capability to produce 15,000 t in Riceboro poly(acrylamide) line.

^e10,000 t of this capacity is suspension polymer.

^f10,000 t of this capacity is suspension polymer. Total capacity includes 27,000 t/yr for Singapore for 1998.

^gEstimated.

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3.2. SOLUTION EFFECT ON

3.2.1. Introduction

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small in the major populated countries of Asia. Current manufacturers of acrylate-based superabsorbents in the United States include The Dow Chemical Co., Hoechst Celanese Corp., under a license from Sanyo Chemical Industries,⁷ NA Industries (a subsidiary of Nippon Shokubai Co., Ltd.), AMCOL International (Chemdal), and Stockhausen GMBH. AMCOL has recently added significant manufacturing capacity both in Europe and in the United States. European superabsorbent manufacturers include AMCOL, Stockhausen GMBH, Dow, Hoechst Casella, Allied Colloids, Ltd., and BASF Aktiengesellschaft in partnership with Nippon Shokubai.⁸ Japanese producers include Nippon Shokubai, Sanyo, Mitsubishi Petrochemical Co., Ltd., Kao Soap, and Sumitomo Seika. There are also a number of smaller producers in the United States, Europe, and the Far East. Elf Atochem S.A., Sumitomo Seika, and Kao Soap have been the three most prominent users of a suspension process to make superabsorbent polymers.

The synthesis and use of crosslinked, partially neutralized, polyacrylate superabsorbents have been the subject of several reviews^{1,2,9-11}; however, very little information about manufacturing processes has been given. Perhaps the most unique, and arguably the first, commercial process is the polymerization technology patented by Sanyo¹² and licensed⁷ to the Hoechst companies. Acrylic acid, in aqueous solution, was simultaneously polymerized, crosslinked and grafted to starch, and then neutralized and dried. Over the last 10 years, the dominant commercial technology for manufacturing superabsorbents has been solution polymerization of partially neutralized acrylic acid in the presence of a crosslinker using free-radical initiators, typically without a graft substrate. The resultant hydrogel is dried and ground to the desired particle size. Reverse-phase suspension polymerization is also practiced, but volumes produced are small relative to those from solution polymerization.

In this chapter, aspects of polymerization technology are reviewed, emphasizing commercial practice. While the review of the patent documents is intended to be thorough, it is not exhaustive. Our hope is to provide some insight into the interaction of engineering and chemistry in the design and implementation of commercial processes for the manufacture of superabsorbent polymers.

3.2. SOLUTION POLYMERIZATION: UNIT OPERATIONS AND THEIR EFFECT ON PRODUCT QUALITY

3.2.1. Introduction to Solution Polymerization Processes

3.2.1.1. Scale-Up Considerations. The initial development of a new superabsorbent polymer typically takes place at the laboratory scale, employing from a few grams up to several hundred grams of reactants. As with other polymeric products, it is convenient to think about the chemistry of the superabsorbent polymerization process as chemistry at the parts per thousand or parts per million scale (ppm). Polymerization initiators and crosslinkers are used at levels ranging from a few tens of ppm to several thousand ppm. Impurities in the monomer can have a strong effect on both the polymerization process and product quality. For example, the inhibitor methyl ether of hydroquinone (MEHQ), acrylic acid dimer discussed in Chapter 2,